

SPECIFICATION

METHOD OF PRODUCING CARBON FIBER,
CATALYST STRUCTURE AND MEMBRANE ELECTRODE
ASSEMBLY FOR SOLID POLYMER FUEL CELL

TECHNICAL FIELD

[0001] This invention relates to a method of producing carbon fibers, a novel catalyst structure using the carbon fibers obtained by this method, a membrane electrode assembly for solid polymer fuel cell 5 using the catalyst structure and a solid polymer fuel cell provided with the membrane electrode assembly for solid polymer fuel cell, and more particularly to a method of producing fibril-shaped carbon fibers, which are high in the residual carbon ratio and excellent in the electric 10 conduction and suitable as a carrier or the like for a filler and a noble metal catalyst combined with an electrode material, a polymer or the like to provide a reinforcement and a functionality, and a novel catalyst structure improving a utility ratio of the noble metal catalyst to be supported.

BACKGROUND ART

[0002] As the carbon fiber have hitherto been known pitch-based carbon fiber obtained by liquid phase carbonization, polyacrylonitrile- and rayon-based carbon fibers obtained by solid phase carbonization, vapor-growth carbon fiber obtained by vapor phase carbonization, carbon nanotubes obtained by laser process or arc discharge process, 15 and the like. In the production steps of the pitch-based carbon fiber, polyacrylonitrile-based carbon fiber and rayon-based carbon fiber, it is necessary to take a spinning step for obtaining a fibrous precursor, so that the production steps become complicated and it is difficult to obtain fibers having a size finer than 1 μm . In the production of the vapor-growth carbon fiber, there is a problem that it is not necessarily 20 said to establish a mass production process because the production instrument is expensive and the yield is not high and the like. Even 25 in the production of the carbon nanotubes, the production instrument is

expensive and the efficient mass production technique is now examining and there is a problem that it is difficult to obtain fibers having a size of more than 0.1 μm .

5 [0003] On the contrary, JP-A-5-178603 discloses a production method of carbonaceous powder without requiring an infusion step wherein it is possible to control the electric characteristics such as electric conductivity and the like and the residual carbon ratio is high and the electric conduction is excellent. In this method, however, polyaniline powder is used as a starting material, so that the carbon 10 fiber is never obtained without the spinning step.

15 [0004] Lately, fuel cells are caught the attention of as a cell having a high power generation efficiency and a small environmental burden, and the research and development thereof are widely made. Among the fuel cells, solid polymer fuel cells are high in the power density and low in the working temperature and easy in the miniaturization and cost reduction as compared with the other type fuel cells, so that they are expected to become widely used as a power source for electric cars, a dispersion power generation system and a household cogeneration system.

20 [0005] In general, the solid polymer fuel cell comprises a membrane electrode assembly in which catalyst layers having a noble metal catalyst are arranged on both faces of a solid polymer electrolyte film and a carbon paper, carbon cloth or the like is disposed on an outside of the catalyst layer as a gas diffusing layer. Furthermore, an 25 electrically conductive separator provided with gas flowing channels is disposed on the outside of the diffusing layer. Such a separator plays a role for passing a fuel gas or an oxidizer gas and for conducting a current from the gas diffusing layer having a function of current collector to take out electric energy.

30 [0006] Heretofore, the catalyst layer mainly comprises a catalyst structure formed by supporting a noble metal catalyst on granular carbon and a polymer electrolyte, and is prepared by forming a paste or a slurry of a catalyst structure, a polymer electrolyte and an organic

solvent on a carbon paper or the like through a screen printing process, a deposition process, a spraying process or the like, or by forming the paste or slurry on a previously provided substrate in the form of a sheet and then transferring onto the solid polymer electrolyte

5 membrane through hot press or the like. The polymer electrolyte included in the catalyst layer has a function of dissolving hydrogen diffused from the gas diffusion layer, and a polymer having an excellent ion conduction such as ion exchange resin or the like is usually used (edited by The Chemical Society of Japan, "Chemical

10 review No. 49, Material Chemistry of New Type Cells", Institute Publishing Center, 2001, p.180-182; "Solid Polymer Fuel Cells <2001>", The Technical Information Society, 2001, p.14-15).

[0007] The catalyst structure is formed by supporting a noble metal on nano-porous granular carbon having pores such as meso-pores or

15 the like. However, the polymer electrolyte can not penetrate into these pores, and hence the noble metal supported in the pores can not contact with the polymer electrolyte. As a result, in the conventional catalyst structure using the granular carbon as a carrier, there is a problem that the utility ratio of the noble metal is considerably low.

20 [0008] Also, hydrogen as a fuel is dissociated into proton and electron on the noble metal and the resulting electron must be moved through carbon to the diffusing layer functioning as a current collector. As a result, there is a problem that the noble metal supported on the carbon being insufficient in the contact between carbons and having no

25 electrical continuity to the current collector is not effectively utilized and hence the dissociation of hydrogen does not proceed sufficiently.

DISCLOSURE OF THE INVENTION

[0009] It is, therefore, an object of the invention to solve the problems of the conventional techniques and to provide a method of

30 producing carbon fibers wherein the spinning step and infusion step are not required and the residual carbon ratio is high and the electric conduction is excellent and carbon fibers having a fiber size of 30 to few hundreds nm can be obtained efficiently and it is possible to

control the electric characteristics such as electric conductivity of the resulting carbon fiber and the like.

5 [0010] Also, it is another object of the invention to provide a catalyst structure improving the utility ratio of a noble metal catalyst, a membrane electrode assembly for solid polymer fuel cell using the same, and a solid polymer fuel cell provided therewith.

10 [0011] The inventors have made various studies in order to achieve the above objects, and found that carbon fibers capable of controlling the electric characteristics such as electric conductivity and the like and being high in the residual carbon ratio and excellent in the electric conduction and having a fiber size of 30 to few hundreds nm can be efficiently produced by using a fibril-shaped polymer made from a compound having an aromatic ring as a starting material without requiring the spinning step and the infusion step.

15 [0012] Further, the inventors have found that a noble metal can be carried on only the surface of the carbon fiber by supporting a noble metal catalyst on the carbon fiber and the utility ratio of the noble metal can be improved because the carbon fiber is three-dimensionally continuous and is excellent in the electric conduction.

20 [0013] That is, the production method of the carbon fiber according to the invention is characterized in that a compound having an aromatic ring is oxidative-polymerized to obtain a fibril-shaped polymer and then the fibril-shaped polymer is fired in a non-oxidizing atmosphere.

25 [0014] In a preferable embodiment of the production method of the carbon fiber according to the invention, the compound having the aromatic ring is a compound having a benzene ring or an aromatic heterocyclic ring. In this case, the compound having the aromatic ring is particularly preferable to be at least one compound selected from the group consisting of aniline, pyrrole, thiophene and derivatives thereof.

30 [0015] In another preferable embodiment of the production method of the carbon fiber according to the invention, the oxidative-polymerization is an electrolytic oxidative-polymerization.

[0016] Also, the catalyst structure according to the invention is characterized in that fine particles of a noble metal are supported on the carbon fibers produced by the above method. That is, the catalyst structure according to the invention comprises the noble metal as a catalyst and the carbon fibers as a carrier in which the carbon fibers are three-dimensionally continuous.

5 [0017] In a preferable embodiment of the catalyst structure according to the invention, the fine particles of the noble metal are supported on the carbon fibers through an electroplating.

10 [0018] In another preferable embodiment of the catalyst structure according to the invention, the noble metal includes at least Pt.

15 [0019] Furthermore, the membrane electrode assembly (MEA) for solid polymer fuel cell according to the invention is a membrane electrode assembly comprising a solid polymer electrolyte membrane, catalyst layers arranged on both sides of the solid polymer electrolyte membrane, and a diffusing layer arranged on one side of the catalyst layer, characterized in that the catalyst layer comprises the above catalyst structure and a polymer electrolyte.

20 [0020] Moreover, the solid polymer fuel cell according to the invention is characterized by providing the above membrane electrode assembly.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 is a SEM photograph of a fibril-shaped polyaniline produced in Example 1 (before firing).

25 [0022] FIG. 2 is a SEM photograph of carbon fibers produced in Example 1 (after firing).

[0023] FIG. 3 is a SEM photograph of three-dimensionally continuous carbon fibers produced in Example 3.

30 [0024] FIG. 4 is a SEM photograph three-dimensionally continuous carbon fibers supported with platinum (catalyst structure) prepared in Example 3.

[0025] FIG. 5 is a graph showing voltage-current characteristics of solid polymer fuel cells of Example 3 and Comparative Example 2.

BEST MODE FOR CARRYING OUT THE INVENTION

[0026] The invention will be described in detail below.

[0027] <Production method of carbon fibers>

The production method of carbon fibers according to the
5 invention is characterized by (i) oxidative-polymerizing a compound
having an aromatic ring to obtain a fibril-shaped polymer and (ii)
firing the fibril-shaped polymer in a non-oxidizing atmosphere.

In the production method of carbon fibers according to the invention,
the spinning step and the infusion step are not required, so that the
10 number of steps is small and the productivity is excellent and the cost
becomes cheap.

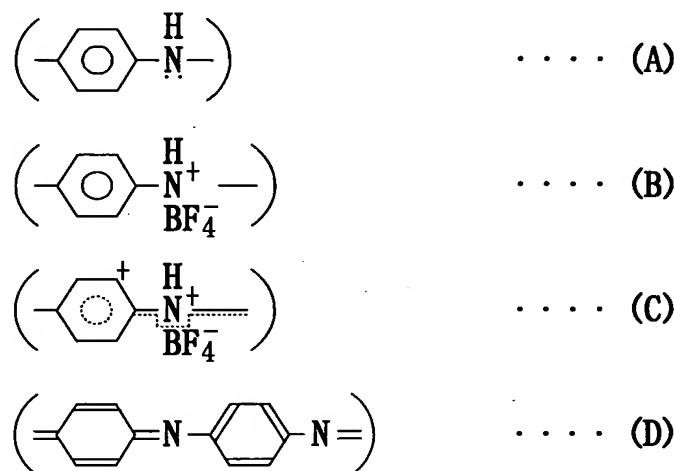
[0028] As the compound having the aromatic ring used in the
production method of carbon fibers according to the invention may be
mentioned compounds having a benzene ring and compounds having an
15 aromatic heterocyclic ring. As the compound having the benzene ring
are preferable aniline and aniline derivatives. As the compound
having the aromatic heterocyclic ring are preferable pyrrole, thiophene
and derivatives thereof. These compounds having the aromatic ring
may be used alone or in a combination of tow or more.

20 [0029] In the production method of carbon fibers according to the
invention, the compound having the aromatic ring is oxidative-
polymerized to obtain a fibril-shaped polymer. The fibril-shaped
polymer has a diameter of 30 to few hundreds nm, preferably 40-500
nm and a length of 0.5-100000 μ m, preferably 1-10000 μ m.

25 [0030] As the oxidative-polymerization are mentioned an
electrolytic oxidative-polymerization method and a chemical
oxidative-polymerization method, but the electrolytic oxidative-
polymerization method is preferable. In the oxidative-polymerization,
it is preferable to intermingle the compound having the aromatic ring
30 as a starting material with an acid. In this case, a negative ion of the
acid is incorporated into the synthesized fibril-shaped polymer as a
dopant to provide a fibril-shaped polymer having an excellent electric
conduction, and finally the electric conduction of the carbon fiber can

be further improved by using such a fibril-shaped polymer.

[0031] This point is further described in detail. For example, when aniline is used as a starting polymerization material, a polyaniline obtained by oxidative-polymerizing aniline at a state of intermingling 5 with HBF_4 is usually existent at a state of mixing four kinds of polyanilines represented by the following formulae (A)-(D):



, that is, a mixed state of a benzonoid=amine state (formula A), a benzonoid=ammonium state (formula B), a dope=semiquinone radical state (formula C) and a quinoid=diimine state (formula D). In this 10 case, the mixing ratio of these states is not particularly limited, but the residual carbon ratio and electric conductivity of the finally obtained carbon fiber become high in the state containing a greater part of the dope=semiquinone radical state (formula C) as compared with the state containing a greater part of the quinoid=diimine state (formula D). Therefore, in order to obtain polyaniline containing a greater part of 15 the dope=semiquinone radical state (formula C), the acid is preferable to be intermingled in the polymerization. Moreover, the acid intermingled in the polymerization is not limited to HBF_4 , but various acids can be used. In addition to HBF_4 can be exemplified H_2SO_4 , 20 HCl , HClO_4 and the like. In this case, the concentration of the acid is preferably 0.1-3 mol/L, more preferably 0.5-2.5 mol/L.

[0032] The mixing ratio (doping level) of the dope=semiquinone

radical state (formula C) can be adjusted properly. By adjusting such a mixing ratio (doping level) can be controlled the residual carbon ratio and electric conductivity of the resulting carbon fiber. As the doping level is made higher, the residual carbon ratio and electric 5 conductivity of the resulting carbon fiber become high. Moreover, the mixing ratio (doping level) of the dope=semiquinone radical state (formula C) is not particularly limited, but is preferable to be usually within a range of 0.01-50%.

[0033] In case of obtaining the fibril-shaped polymer through the 10 electrolytic oxidative-polymerization, a pair of electrode plates as a working electrode and a counter electrode are immersed in a solution containing the compound having the aromatic ring, and then a voltage of not less than an oxidation potential of the compound having the aromatic ring is applied between both the electrodes or a current 15 capable of ensuring a voltage enough to polymerize the compound having the aromatic ring is flowed, whereby the fibril-shaped polymer is formed on the working electrode. As one example of the method of synthesizing the fibril-shaped polymer through the electrolytic oxidative-polymerization, there is exemplified a method wherein plates 20 or porous materials made from a good conductive substance such as stainless steel, platinum, carbon or the like are used as the working electrode and the counter electrode, and immersed in an electrolyte solution containing an acid such as H_2SO_4 , HBF_4 or the like and a compound having an aromatic ring, and then a current of 25 0.1-1000 mA/cm², preferably 0.2-100 mA/cm² is flowed between both the electrodes to precipitate a fibril-shaped polymer on the working electrode, or the like. In this case, the concentration of the compound having the aromatic ring in the electrolyte solution is preferably 0.05-3 mol/L, more preferably 0.25-1.5 mol/L. To the 30 electrolyte solution may be properly added a soluble salt or the like for adjusting pH in addition to the above components.

[0034] As mentioned above, the electric conductivity and residual carbon ratio of the resulting carbon fiber can be controlled by

adjusting the doping level of the carbon fiber, but the method of adjusting the doping level is not particularly limited as long as the resulting fibril-shaped polymer is subjected to a reduction treatment through any process. As a concrete example, there are mentioned a 5 method of immersing in an aqueous solution of ammonia or an aqueous solution of hydrazine, a method of electrochemically applying a reduction current, and the like. The control of the dopant quantity included in the fibril-shaped polymer can be carried out by the reduction level, in which the dopant quantity in the fibril-shaped 10 polymer is decreased by the reduction treatment. Also, the doping level can be adjusted to a certain extent by controlling the acid concentration in the polymerization stage, but it is difficult to obtain various samples having largely different doping levels, so that the above reduction method is preferably used. Moreover, the dopant 15 having the thus adjusted content is kept in the carbon fibers obtained by controlling the firing conditions even after the firing as mentioned later, whereby the electric conductivity and residual carbon ratio of the carbon fiber are controlled.

[0035] The fibril-shaped polymer obtained on the working electrode 20 is washed with water or a solvent such as an organic solvent or the like, dried and carbonized by firing in a non-oxidizing atmosphere to obtain fibril-shaped, three-dimensionally continuous carbon fibers. The drying method is not particularly limited, but there can be exemplified air-drying, vacuum drying and a method using a fluidized bed drying 25 device, flash drier, spray drier or the like. Also, the firing conditions are not particularly limited, but may be set so as to provide an optimum electric conductivity in accordance with the application of the carbon fiber. Particularly, in case of requiring the high electric conductivity, it is preferable that the temperature is 500-3000°C, preferably 600- 30 2800°C and the time is 0.5-6 hours. Moreover, as the non-oxidizing atmosphere may be mentioned an inert gas atmosphere such as a nitrogen atmosphere, an argon atmosphere, a helium atmosphere or the like, and in some cases may be used a hydrogen atmosphere.

[0036] The carbon fibers obtained by the method of the invention have a diameter of 30 to few hundreds nm, preferably 40-500 nm, a length of 0.5-100000 μm , preferably 1-10000 μm , and a surface resistance of $10^6\text{-}10^{-2} \Omega$, preferably $10^4\text{-}10^{-2} \Omega$. Also, the carbon fibers have a residual carbon ratio of 95-30%, preferably 90-40%.
5 The carbon fibers are high in the electric conduction as compared with the granular carbon because the carbon as a whole has a three-dimensionally continuous structure.

[0037] <Catalyst structure>
10 The catalyst structure according to the invention is characterized by supporting fine particles of a noble metal on the carbon fibers produced by the above method. The carbon fiber is excellent in the contacting property with a polymer electrolyte because fine particles of the noble metal precipitate on surface portions of the
15 carbon fibers capable of permeating the polymer electrolyte. Therefore, the fine particles of the noble metal supported on the carbon fibers are high in the contacting ratio with the polymer electrolyte as compared with the conventional one. Also, the carbon fibers are high in the electric conduction as compared with the granular carbon
20 because they are three-dimensionally continuous. From these reasons, the catalyst structure according to the invention is considerably low in the ratio of (i) noble metal not contacting with the polymer electrolyte and (ii) noble metal supported on the isolated carrier not electrically conducting to the current collector as compared with the conventional
25 catalyst structure, so that the utility ratio of the noble metal is highly improved. Moreover, the catalyst structure according to the invention is effective as a catalyst for various chemical reactions, but can be preferably used in a catalyst layer for the solid polymer fuel cell.

[0038] As the noble metal used in the catalyst structure according to
30 the invention is particularly preferable Pt. In the invention, Pt may be used alone or may be used as an alloy with another metal such as Ru or the like. By using Pt as a noble metal can be oxidized hydrogen in a high efficiency even at a low temperature of not higher than 100°C.

By using the alloy of Pt with Ru or the like can be prevented the poisoning of Pt with CO to prevent the lowering of the catalyst activity. Moreover, the particle size of the fine particles of the noble metal supported on the carbon fibers is preferably within a range of 5 0.5-20 nm, and the supporting ratio of the noble metal is preferably within a range of 0.05-5 g per 1 g of the carbon fibers.

[0039] As the method of supporting the noble metal on the carbon fibers are mentioned an impregnation method, an electroplating method (electroreduction method), an electroless plating method and the like, 10 but the electroplating method is preferable in a point that the adjustment of the ratio of the noble metal supported is easy. In the electroplating method, the noble metal is electrochemically precipitated from a solution dissolving a target noble metal such as aqueous solution of chloroplatinate, whereby the noble metal can be precipitated on only 15 the surface of the carbon fiber and the precipitating amount can be accurately controlled by an electric charge amount applied. In this case, the particle size, form, adhesion state and the like of the fine particles of the noble metal precipitated can be changed by properly selecting the current applying conditions (current density, direct 20 current process or pulse process, temperature, concentration of noble metal ion, kind of co-existing ion and the like).

[0040] <Membrane electrode assembly for solid polymer fuel cell>
The membrane electrode assembly (MEA) for the solid polymer fuel cell according to the invention comprises a solid polymer electrolyte film, a catalyst layer arranged on each side of the solid polymer electrolyte film and a diffusing layer arranged on one side of the catalyst layer, in which the catalyst layer comprises the aforementioned catalyst structure and a polymer electrolyte. In the membrane electrode assembly, the amount of the noble metal in the 25 catalyst layer can be considerably decreased as compared with the conventional one. In the membrane electrode assembly according to the invention, therefore, the cost becomes largely cheap as compared 30 with the conventional one.

[0041] In the solid polymer electrolyte film can be used an ion-conductive polymer. As the ion-conductive polymer may be mentioned a polymer having an ion exchanging group such as sulfonic acid, carboxylic acid, phosphonic acid, phosphonous acid or the like, in which the polymer may contain or may not contain fluorine. As the ion-conductive polymer are mentioned perfluorocarbon sulfonic acid based polymers and the like such as Naphion (registered trade mark) and so on.

[0042] The catalyst layer comprises the catalyst structure and the polymer electrolyte. As the polymer electrolyte can be used the ion-conductive polymer used in the solid polymer electrolyte film. The thickness of the catalyst layer is not particularly limited, but is preferably within a range of 0.1-100 μm . The ratio of the catalyst structure and the polymer electrolyte in the catalyst layer is preferable to be within a range that the polymer electrolyte is 10-500 parts by mass per 100 parts by mass of the catalyst structure. Also, the supporting amount of the noble metal in the catalyst layer is determined by the supporting ratio and the thickness of the catalyst layer, and is preferably within a range of 0.001-0.8 mg/cm^2 .

[0043] The diffusing layer is a layer for feeding a hydrogen gas or an oxidizer gas such as oxygen, air or the like to the catalyst layer to give and receive the resulting electron, and also plays a role as a current collector. The material used in the diffusing layer is not particularly limited as long as it is porous and has an electron conduction, and includes porous carbon cloth, carbon paper and the like.

[0044] The membrane electrode assembly according to the invention is not particularly limited, but can be produced by forming fibril-shaped carbon fibers on a diffusing layer made of a carbon paper or the like, supporting fine particles of a noble metal such as platinum or the like on the carbon fibers through an electroplating or the like, applying a solution containing a polymer electrolyte such as Naphion (registered trade mark) or the like to the noble metal supported carbon fibers to form a catalyst layer, sandwiching the solid polymer

electrolyte film made of Naphion or the like between the catalyst layers and subjecting to a heating treatment. In this case, the step of applying the catalyst structure can be omitted.

[0045] <Solid polymer fuel cell>

5 Further, the solid polymer fuel cell according to the invention is characterized by providing the above membrane electrode assembly. The solid polymer fuel cell of the invention is not particularly limited in addition to the provision of the membrane electrode assembly, and can be produced likewise the conventional solid polymer fuel cell.

10 The solid polymer fuel cell according to the invention has merits that the utility ratio of the noble metal such as Pt or the like used in the catalyst layer is high, and the use amount thereof is less and the cost becomes cheap.

[0046] <Examples>

15 The following examples are given in illustration of the invention and are not intended as limitations thereof.

[0047] (Example 1)

20 A working electrode made of a platinum plate is placed in an acidic aqueous solution containing 1.0 mol/L of aniline monomer and 2.0 mol/L of HBF_4 , and a platinum plate is used as a counter electrode, and the electrolytic polymerization is carried out at room temperature and a constant current of 25 mA/cm^2 for 30 minutes to electrodeposit polyaniline on the working electrode. The resulting polyaniline film is sufficiently washed with an ion exchanged water and air-dried over 25 a day and further dried under vacuum for 24 hours to obtain polyaniline. As observed through SEM, it is confirmed to obtain polyaniline fibrils having a diameter of 100-200 nm at an entangled state. A photograph thereof is shown in FIG. 1. At top right and bottom left of the photograph are shown the polyaniline fibrils according to the invention.

30 **[0048]** The polyaniline is subjected to a firing treatment by heating up to 1200°C at a temperature rising rate of $2.5^\circ\text{C}/\text{min}$ in an Ar atmosphere and then keeping 1200°C for 1 hour. As the fired product is observed through SEM, it is confirmed that the diameter is 100-200 nm,

and carbon fibers having substantially the same form as that before the firing treatment are obtained. A photograph thereof is shown in FIG. 2. At bottom right and bottom left of this photograph is shown the fibril-shaped carbon fiber according to the invention.

5 [0049] (Example 2)

A working electrode made of a carbon paper (made by Toray Industries, Inc.) is placed in an acidic aqueous solution containing 0.5 mol/L of aniline monomer and 1.0 mol/L of HBF_4 , and a platinum plate is used as a counter electrode, and the electrolytic polymerization 10 is carried out at room temperature and a constant current of 10 mA/cm^2 for 2 minutes to electrodeposit polyaniline on the working electrode. The resulting polyaniline is washed with an ion exchanged water and dried under vacuum for 24 hours. As observed through SEM, it is confirmed that fibril-shaped polyaniline having a diameter of 50-15 100 nm is obtained on carbon fibers constituting the carbon paper.

[0050] The polyaniline is subjected to a firing treatment by heating up to 900°C at a temperature rising rate of $3^\circ\text{C}/\text{min}$ in an Ar atmosphere and then keeping 900°C for 1 hour. As the fired product is observed through SEM, it is confirmed that carbon fibers having a diameter of 20 40-100 nm are obtained on the carbon paper.

[0051] (Comparative Example 1)

Phenol beads (UA-30) are used as a starting material and subjected to a firing treatment by heating up to 800°C at a temperature rising rate of $3^\circ\text{C}/\text{min}$ in a nitrogen atmosphere and then keeping 25 800°C for 1 hour, and then the resulting carbon material (fired product) is pulverized to obtain carbonaceous powder.

[0052] With respect to the thus obtained carbon fibers and carbonaceous powder, the residual carbon ratio is measured. Also, each of the carbon fibers and carbonaceous powder is press-shaped 30 into pellets and then the surface resistance is measured by a surface resistance meter (Loresta IP or Hiressta IP, made by Mitsubishi Yuka Co., Ltd.).

[0053]

Table 1

	Residual carbon ratio (%)	Surface resistance (Ω)
Example 1	65	0.2
Example 2	70	1.0
Comparative Example 1	40	1×10^2

[0054] As seen from Table 1, the carbon fibers of the examples are excellent in the electric conduction because the residual carbon ratio is high and the surface resistance is low as compared with those of the 5 comparative example.

[0055] (Example 3)

A working electrode made of a carbon paper (made by Toray Industries, Inc.) is placed in an acidic aqueous solution containing 0.5 mol/L of aniline monomer and 1.0 mol/L of HBF_4 , and a platinum 10 plate is used as a counter electrode, and the electrolytic polymerization is carried out at room temperature and a constant current of 10 mA/cm^2 for 10 minutes to electrodeposit polyaniline on the working electrode. The resulting polyaniline is washed with an ion exchanged water and dried under vacuum for 24 hours. As observed through SEM, it is 15 confirmed that fibril-shaped polyaniline having a diameter of 50-100 nm is obtained on a side of the carbon paper facing to the platinum plate.

[0055] The polyaniline is subjected together with the carbon paper to a firing treatment by heating up to 950°C at a temperature rising rate 20 of $3^\circ\text{C}/\text{min}$ in an Ar atmosphere and then keeping 950°C for 1 hour. As the fired product is observed through SEM, it is confirmed that fibril-shaped three-dimensionally continuous carbon fibers having a diameter of 40-100 nm are formed on the carbon paper. A SEM photograph of the resulting carbon fibers is shown in FIG. 3. 25 Moreover, the carbon fibers have a residual carbon ratio of 45% and a

surface resistance of 1.0 Ω (measured through Loresta IP or Hiressta IP made by Mitsubishi Yuka Co., Ltd.).

[0056] The carbon paper having the carbon fibers on its surface is placed in an aqueous solution of 3% by mass of chloroplatinate as a 5 working electrode, and a platinum plate is used as a counter electrode, and the electroplating (electrolytic reduction) is carried out at a room temperature and a constant current of 30 mA/cm² for 25 seconds to precipitate platinum on the carbon fibers, whereby a catalyst structure having a platinum supporting amount of 0.4 mg/cm² is formed on the 10 carbon paper. In this case, the working electrode and the platinum plate are arranged so that a face of the carbon fibers adhered to the carbon paper is faced to the platinum plate. A SEM photograph of the carbon fibers supported with platinum is shown in FIG. 4.

[0057] A solution of 5% by mass of Naphion (registered trade mark) 15 is applied to the catalyst structure formed on the carbon paper and dried to form a catalyst layer on the carbon paper. Then, the carbon paper provided with the catalyst layer is arranged so as to contact the catalyst layer with each face of a solid polymer electrolyte film made of Naphion (registered trade mark) (film thickness: 175 μm), which are 20 hot-pressed to prepare a membrane electrode assembly (MEA). In the thus obtained membrane electrode assembly, the thickness of the catalyst layer is 10 μm , and a ratio of catalyst structure/Naphion (by mass) is 4/1. The membrane electrode assembly is incorporated into a test cell made of Electro Chemical Co., Ltd. (EFC25-01SP) to 25 prepare a fuel cell. The voltage-current characteristic of the fuel cell is measured under conditions that H₂ flow rate is 300 cm³/min, O₂ flow rate is 300 cm³/min, cell temperature is 80°C and humidity temperature is 80°C. The result is shown in FIG. 5.

[0058] (Comparative Example 2)

30 A fuel cell is prepared in the same manner as in Example 3 except that MEA made by Electro Chemical Co., Ltd. (solid polymer electrolyte film: Naphion film, film thickness: 130 μm , carrier: granular carbon, platinum supporting ratio: 20% by mass, platinum

supporting amount: 1 mg/cm²) is used, and the voltage-current characteristic thereof is measured. The result is shown in FIG. 5.

[0059] As seen from FIG. 5, the solid polymer fuel cell according to the invention shows the cell characteristic equal to that of the conventional one even if the platinum supporting amount is largely decreased, and the utility ratio of platinum is highly improved. Particularly, it is considered that since the solid polymer fuel cell according to the invention is high in the cell voltage at a low current side, the activation polarization is small and the voltage drop resulted from the chemical reaction at the catalyst layer is small.

INDUSTRIAL APPLICABILITY

[0059] According to the invention, carbon fibers having a high residual carbon ratio, an excellent electric conduction and a fiber size of 30 to few hundreds nm can be obtained efficiently without requiring the spinning step and the infusion step, and there can be provided a method of producing carbon fibers capable of controlling the electric characteristics of the resulting carbon body such as electric conductivity and the like.

[0060] Also, according to the invention can be provided a catalyst structure in which the utility ratio of the noble metal is largely improved as compared with the conventional one by supporting the noble metal catalyst on the fibril-shaped three-dimensionally continuous carbon fibers. Further, there can be provided a cheap membrane electrode assembly using such a catalyst structure and a cheap solid polymer fuel cell provided with such a membrane electrode assembly.